THE MECHANISM OF PODZOLISATION

C. BLOOMFIELD

Rothamsted Experimental Station

In considering the mechanism of podzolisation, the essential question is the nature of the agents responsible for mobilising iron in the upper parts of the profile. The nature of the immobilisation processes that occur in the lower parts of the horizon must depend on the form in which sesquioxides are mobilised and enter this region.

It seems generally agreed that some form of organic matter is responsible for the initial mobilisation. The earlier view, which is still current, is that humified organic matter is the active agent in podzolisation, and indeed in the formation of several other soil types. Mattson considered iron to be mobilised as colloidal ferric oxide, with humose matter acting as a protective colloid; the mobilisation and immobilisation processes are thus considered to be purely physical. It is not always clear whether some of the later proponents of the 'humic theory' consider the process to be physical or chemical.

It seems to ~~be~~ me that the large body of work that stems from the foregoing concept suffers from several fundamental objections:

1. The humic/fulvic preparations studied are extracted from soil, usually with sodium hydroxide, and it is not known to what extent the products are artefacts.

2. The action of colloidal humose matter in the soil is usually inferred from the results of experiments with solutions of ferric salts, or with preformed ferric oxide sols. As podzolisation involves the mobilisation of non-colloidal ferric oxide, this approach provides no answer to the fundamental question. I have been unable to detect any such mobilisation of non-colloidal ferric oxide by humose organic matter extracted from soil, and I know of no experimental demonstration of such an action.

3. In connection with podzolisation, the organic matter is usually extracted from podzol B horizons. Apart from the uncertainty about the effect of the extraction procedure on the properties of the extract, the use of B horizon organic matter would be valid only if it were certain that the immobilisation process does not alter the nature of the organic matter that caused the initial mobilisation, and that the mobilising agent is recovered in its original form. This could be true if the process were physical, or if the immobilisation were a quite simple chemical process, as for example, the formation of an insoluble salt of an acid. The possibility that the agents of mobilisation are not retained in the B horizon must also be considered.

I find that whereas humified A_o material has no measurable iron-mobilising action, under an inert atmosphere sterile water extracts of picked or fallen tree leaves readily dissolve hydrous ferric oxide. The decision to study the sterile system was made partly because of the formidable difficulties of reproducing the microbiological conditions of a soil profile in the laboratory, and partly because the chemical processes presumably represent the starting point of the process. Later work suggests that the sterile system is perhaps not altogether irrelevant, as Roger et al (1969) found that whereas ^{14}C-labelled citric acid was rapidly metabolised in the A_1 horizon of a sol brun lessivé, it passed through the A horizon of a podzol to be metabolised in the B horizon.

The use of a reactive artificial hydrous ferric oxide in such experiments has the obvious advantage of giving measurable effects in the shortest time, but it must be remembered that the reactivities of natural forms of the oxide differ widely, and are probably considerably less than that of the artificial material. The Bangor school has shown that the rate natural ferric oxide dissolves differ considerably from soil to soil.

In studying a complex process, it is obviously desirable first to study its constituent parts in isolation, so that in studying mobilisation processes in the soil it is desirable to limit the extent of counteracting sorption effects that soil colloids might be expected to exert. For this reason I used ferric oxide alone, rather than soils, in studying the mobilisation process.

My earlier findings can be summarised as follows (Bloomfield, 1952, 1953, 1954a,b, 1955a):

1. Although there is no qualitative difference between the action of extracts of the leaves of some 15 widely different tree species, there are considerable quantitative differences between their specific iron-dissolving capacities.

2. The specific activities of leaf extracts are correlated with their contents of polyphenols.

3. Reaction products are sorbed on residual ferric oxide. This suggests a possible mechanism for the formation of the podzol B horizon.

4. Clays sorb polyphenols and polysaccharides from leaf extracts, and are thereby strongly dispersed. This could be relevant to the formation of so~~i~~ls lessivés.

5. Iron is dissolved into true solution, reduced to the ferrous form and complexed. All three of these claims have been contested by later workers, who consider that iron is mobilised as colloidal ferric oxide. This view is based on the study of aerobic systems and, if ferrous compounds are formed initially, it is possible that atmospheric oxidation could cause the formation of colloidal ferric materials, and this might be the cause of the discrepancies between our findings.

This possibility was tested by reacting hydrous ferric oxide with leaf extracts, under sterile non-oxidising conditions, with the reaction mixture contained in a cellulose dialysis tube immersed in the appropriate leaf extract. The apparatus is illustrated in Fig.1. Some oxygen diffused through the fermentation traps, and the Cr^{2+} had to be replaced several times during the experiment. To this extent oxygen was not completely excluded and slight reoxidation may have occurred.

Determination of the concentrations of dissolved iron in the dialysed reaction mixture, and in the dialysate, showed that after 3 weeks, with extracts of Scots pine, larch and oak leaves, 96, 98 and 71 per cent respectively of the total dissolved iron was in dialysable, i.e. non-colloidal, form. When the dialysates were aerated for several days, in the presence of toluene, the contents of dialysable iron decreased to about 10 per cent of the original values. (Bloomfield, 1969). The evidence originally presented for the reduction of ferric iron is not conclusive, being based on the use of 2,2'-dipyridyl as the reagent for Fe^{2+}, and

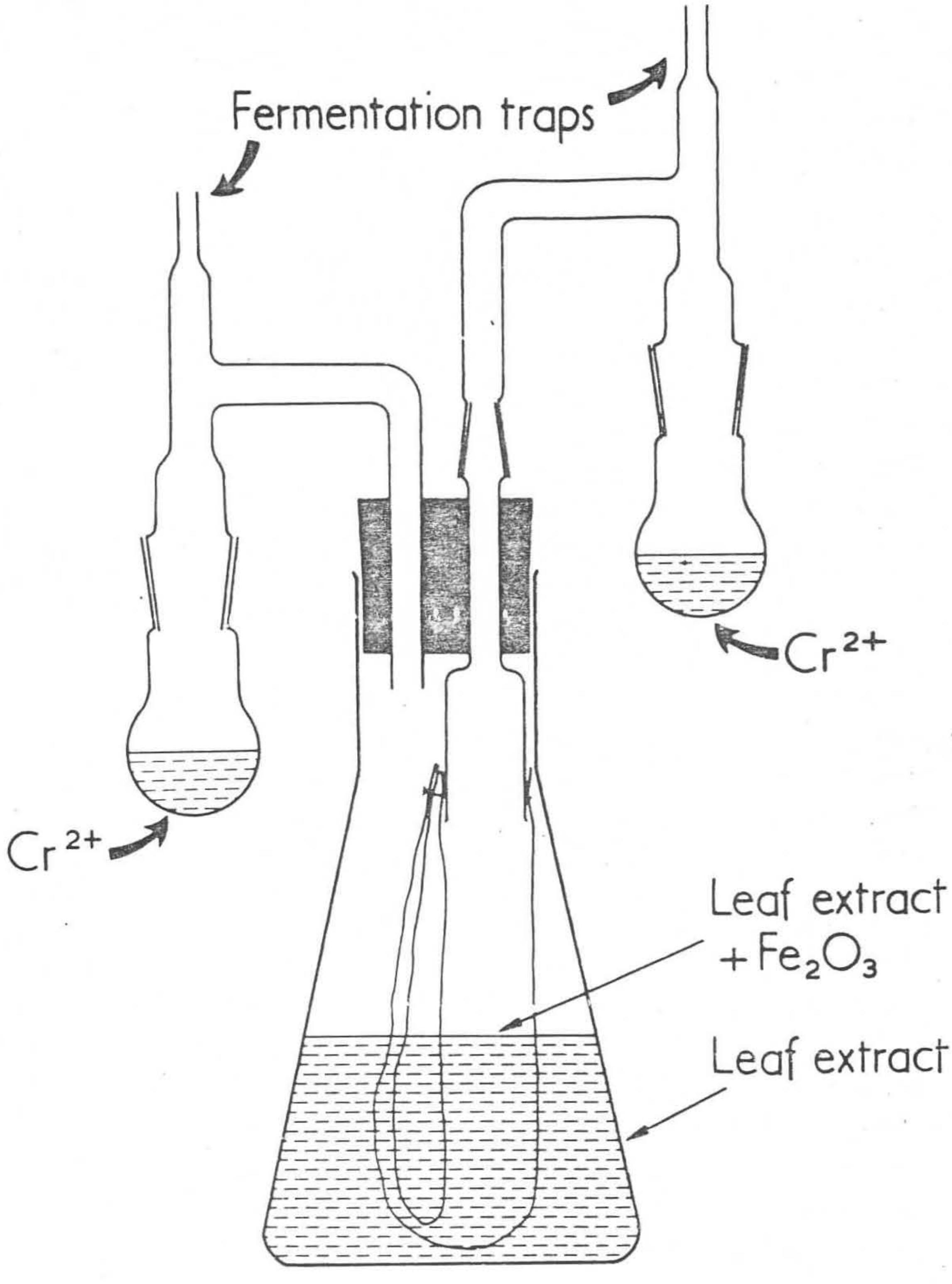

Fig. 1 Apparatus used for reacting hydrous ferric oxide with leaf extracts.

the possibility that Fe^{3+} is reduced by organic matter in the presence of the reagent cannot be ignored. However, it is difficult to explain the effect of aeration on the dialysates other than as the oxidation of ferrous iron.

Extracts of the leaves of broadleaved species seem to be more effective than those of conifers in dissolving ferric oxide, and as podzolisation is most commonly associated with conifers, this is the opposite of what would be expected. However, in some circumstances podzolic soils are formed under broadleaved species, notably the Canadian Grey Wooded soils, which are formed under aspen. Avery (1958) described a micro-podzol formed under beach, and Dimbleby and Gill (1955), and Mackney (1961) discussed the likelihood of podzols forming under oak.

The properties of leaf extracts suggest that all tree species exert a podzolising effect, which suggests, in turn, that opposing influences are usually dominant under broadleaved cover. The action of soil fauna is probably the principal counteracting factor, and it is significant that worms are not present in Grey Wooded soils, or in the micro-podzol described by Avery. The extent to which the litter persists and retains its activity must also be considered in this context (Lossaint, 1959; King and Bloomfield, 1968).

Recent work showed that the iron-dissolving properties of leaf extracts can be affected by the method by which the leaves are dried (King and Bloomfield, 1968). Previously leaves were dried at 105°C in a forced draught, as this induces smaller changes in the phenolic constituents of tea leaves than a slower less drastic treatment. Fig.2 shows that although there is little difference between the properties of undried autumn fallen oak, beech and larch leaves and leaves from the same collections that were freeze- or oven-dried, drying at 105°C considerably increases the activities of picked beech and larch leaves. The quantitative validity of the earlier results for non-deciduous species is thus questionable.

Fig.3 shows the effect of ageing on the activities of picked leaves. In these experiments the amount of iron dissolved by the sterile extract during 4 weeks, under an inert atmosphere, was taken as the measure of activity. Fallen leaves behaved similarly, as did leaves previously irradiated with γ-rays to prevent microbial action (King and Bloomfield, 1968).

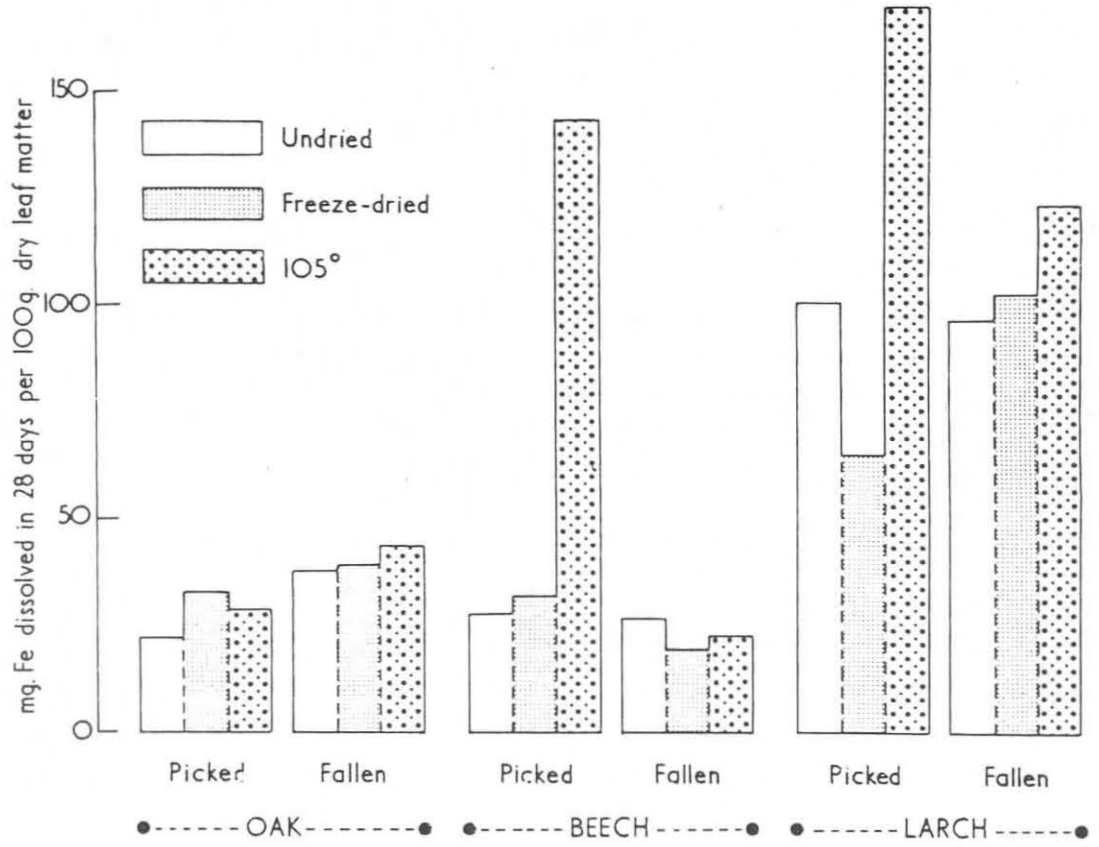

Fig. 2 Comparison of the activity of leaves in dissolving iron oxides.

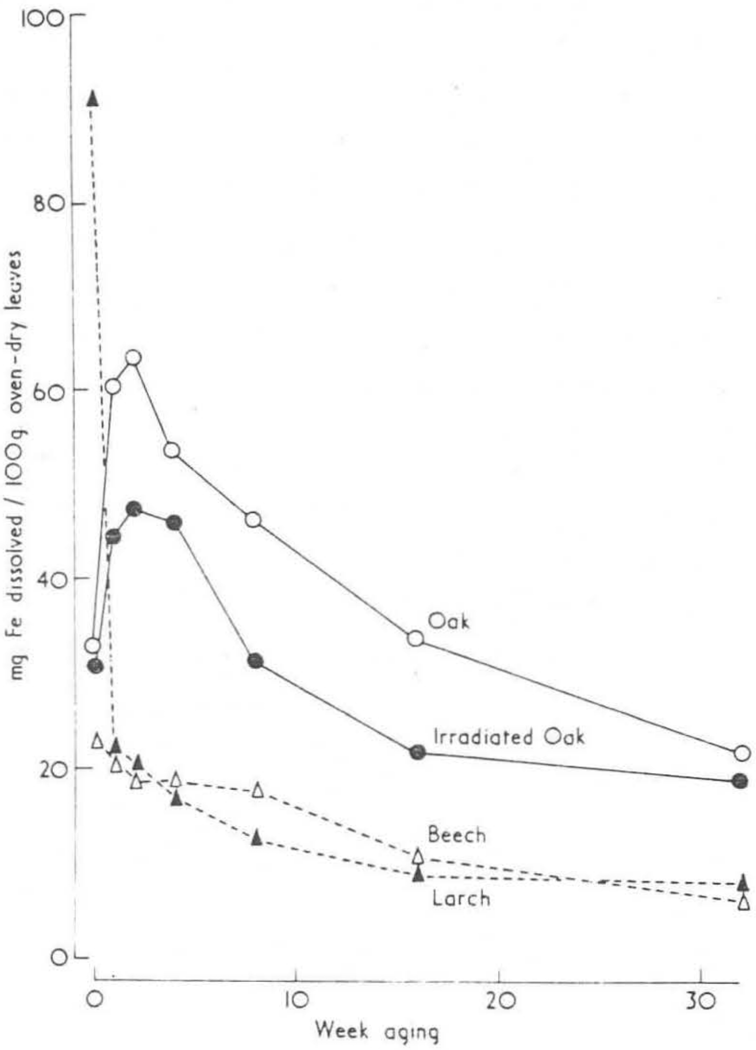

Fig. 3 Effect of ageing on dissolving power of leaves.

It was mentioned earlier that iron dissolved by a leaf extract is sorbed on residual ferric oxide. This effect can be demonstrated by treating a column of ferruginous material, e.g. ferric oxide supported on Kieselguhr, with a leaf extract. Provided the extract is added sufficiently slowly, considerably more than the void volume of the column can be added before the intensely coloured reaction products appear in the effluent. If the column is then allowed to dry slowly from the surface, a passable reproduction of a podzol profile is formed (Bloomfield, 1955b, 1956),

King and Bloomfield (1966) found that polyphenols, sugars, α-amino acids and other nitrogen compounds, and acids, are retained in the columns. The retention of sugars and amino acids seems to be a joint reaction, and recent work shows the reaction to result from the presence of traces of calcium and magnesium carbonates, derived from tap water, in the column fillings No such effect was observed when the columns were previously washed with dilute acid to remove the carbonates.

Although not conceived in connection with the study of podzolisation, current work on the mobilising action of aerobically decomposing plant matter may have some relevance to the role of humose organic matter in the process. In these experiments moist plant matter is incubated aerobically, either alone or with a metal oxide, in the apparatus illustrated in Fig.4. After 2-4 months the distilled water is coloured dark brown by organic matter of large molecular weight that diffuses through the sintered glass plate. The diffusate contains humic and fulvic acids, and small amounts of polysaccharides; so far as can be said at present the darkly coloured colloidal organic components of the diffusates are comparable with the material extracted from soils.

Although the oxides of Cu, Zn, Co, Ni and Pb are quite reactive under these conditions, hydrous ferric oxide is almost inert, and manganese dioxide is only slightly more reactive (Fig.5). This is in complete contrast to the anaerobic system, in which Mn and Fe are two of the most reactive elements (Bloomfield, 1969). Relatively large amounts of the elements seem to combine with the insoluble fibrous plant residues in these experiments, but here again iron behaves differently. The previous value for the amount of iron retained in the residue (Bloomfield, 1969) was far too large, because much Fe was derived from the soil with which the original plant matter was heavily contaminated, and the soil was not

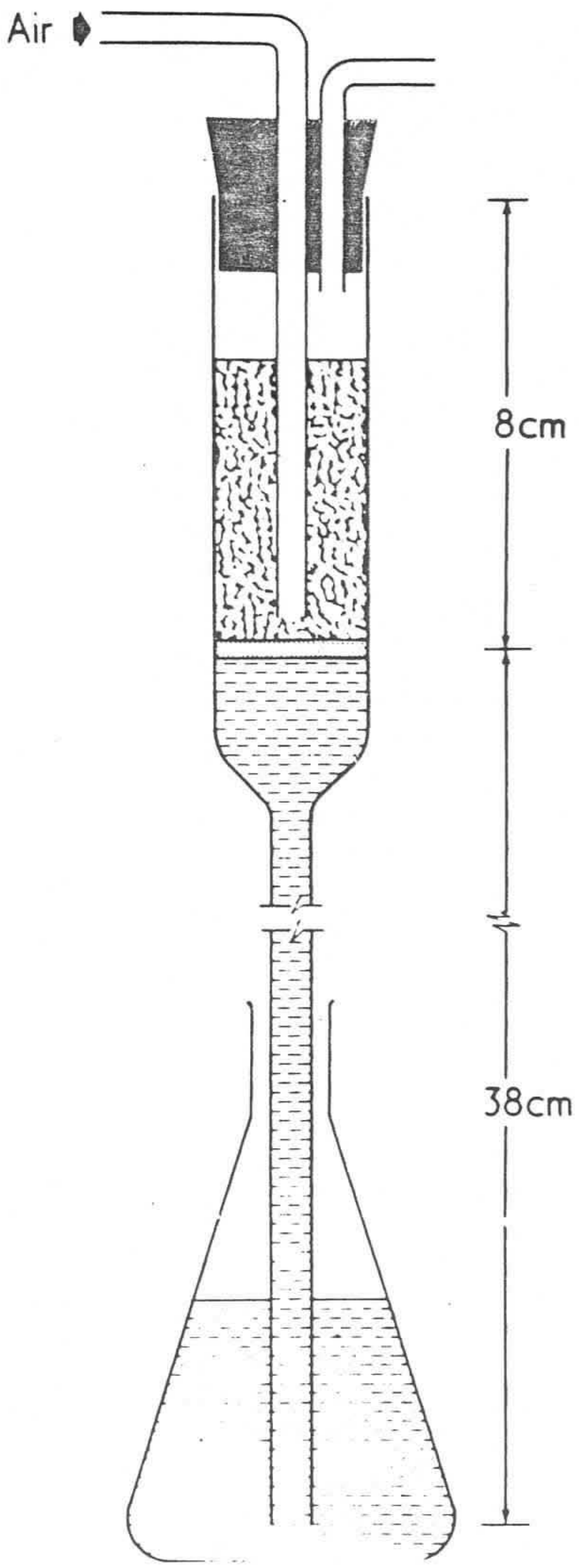

Fig. 4 Aerobic incubation of plant matter.

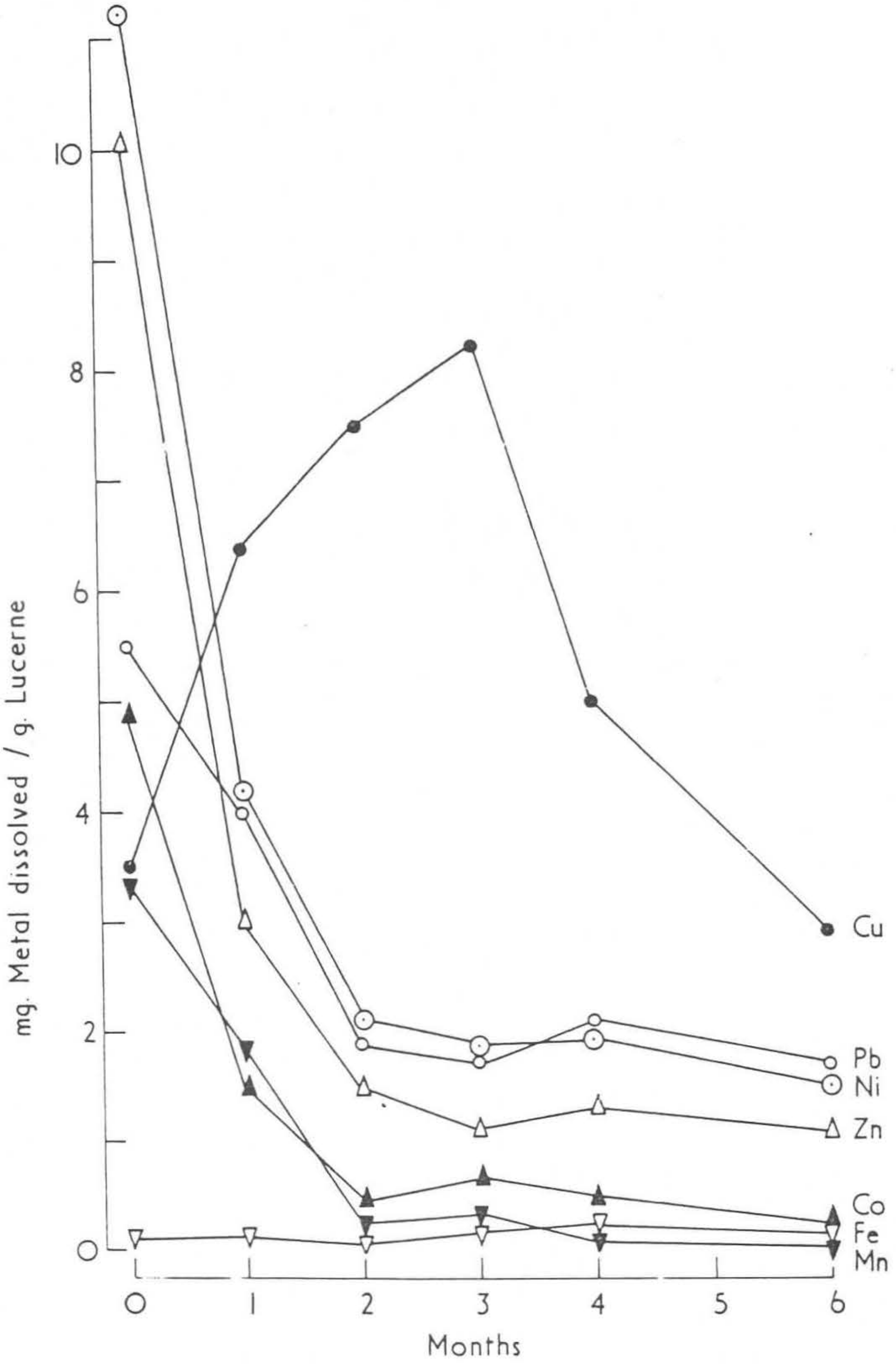

Fig. 5 Metal dissolving capacity of extracts of rotted lucerne

completely removed by the washing and flotation processes to which the residue was subjected. Only about 0.3 mg Fe per g of residue was retained when the experiment was repeated with uncontaminated (sand culture) lucerne. This value compares with 4-5 mg per g for the other elements that were studied.

The metal-dissolving capacities of extracts of rotted lucerne decrease steadily as rotting proceeds, except with Cu, with which the activity increases at first and then decreases rapidly. With iron, as with other elements, the activity of the extract is minimal by the time recognisable humose material has formed, so that the dissolution process seems to result from the action of small molecular weight species that are metabolised as rotting proceeds. These results are summarised in Fig.5. The activity of humose organic matter as an agent of mobilisation seems to be largely confined to its action as an ion exchanger; because the large molecular-weight species are strongly sorbed by soil colloids, these are no doubt of considerable importance in the immobilisation of metals in soils (Bloomfield, Kelso and Piotrowska 1970).

REFERENCES

Avery, B.W. 1958 J.Soil Sci. 9, 210
Bloomfield, C. 1952 Nature 170, 540
" 1953 ibid. 172, 958
" 1953 J. Soil Sci. 4, 5:17
" 1954a ibid. 5, 39; 46; 50
" 1954b Trans. 5th Int. Congr. Soil Sci., Leopoldville, 2, 280
" 1955a J. Soil Sci. 6, 284
" 1955b Chem. & Ind. 1596
" 1956 Trans. 6th Int. Congr. Soil Sci., Paris, 1, 4; 5,3
" 1969 Roth. Ann. Rep. for 1968, p.1, 75
" 1969 Chem. & Ind. 1633
Bloomfield, C., Kelso, W.I. and Piotrowska, M. 1970 Chem. & Ind. (in press)
Dimbleby, C.W. and Gill, J.M. 1955 Forestry 28, 95
King, H.G.C. and Bloomfield, C. 1966 J. Sci. Fd. Agric. 17, 39
" " 1968 J. Soil Sci. 19, 67
Lossaint, P. 1959 Ann. Agron. Paris, 10, 369; 493
Mackney, D. 1961 J. Soil Sci. 12, 23
Roger, P., Bruckert, S. and Jacquin, F. 1969 Sciences du Sol 2, 99

DISCUSSION

R.I. Davies (U.C.N.W. Bangor) enquired how the leaves which Bloomfield used in his experiments were collected, and of their condition at the time of irradiation.

C. Bloomfield in reply stated that they were collected daily, done up in polythene and sent by post for irradiation. Dual samples were sent, but only one irradiated. Leaves were also aged by ~~placing~~ keeping them in large beakers ~~in a cool~~ at room ~~close to field~~ temperature~~s~~. It was stressed that the experiments carried out in the laboratory involved the action of water extracts upon ferric oxide. ~~solutions~~. These extracts would remove iron from the soil if nothing stops them, but care was necessary as different materials would react differently. In the soil, the greater sorptive action of clay would discourage horizon differentiation.

R.I. Davies drew attention to differences between species and also between the same tree species growing on soils with differing nutrient status. With a poor nutrient supply podzols could be observed under beech, but not in the case of more fertile soils.

B. Clayden (Soil Survey, Swansea) spoke of the tendency to characterise podzols by the movement of aluminium, and asked Bloomfield to comment on the part aluminium played as seen in the light of his work.

C.M. Bloomfield observed appreciable mobilisation of aluminium oxide by tree leaf extracts in his early experiments, and this could well be significant in relation to podzolisation. However, because of the possibility that silicate - derived aluminium is included with free alumina in soil extracts, there is some uncertainty in the determination of the latter in soils, and thought the results should be viewed with caution. It is interesting that although hydrous aluminium oxide is mobilised by tree leaf extracts, neither aerobically nor anaerobically decomposing plant matter has any detectable mobilising action on this oxide. In this connection, it is interesting to note that the solubility of Al seems to be decreased in gleyed horizons.

D. Mackney (Soil Survey, Rothamsted) mentioned a 'chemical podzol' described by Duchaufour in which there had been no translocation.

C. Bloomfield questioned this because if there had been no translocation why call it a podzol. Mobilization depends on the base status and also